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μSR Study of Charge Carrier Diffusion in Regioregular Poly(3-butylthiophene-2,5-diyl)

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Abstract

Temperature-dependent of charge carrier diffusion in regioregular-poly(3-butylthiophene-2,5-diyl) (RR-P3BT) has been studied by Longitudinal Field (LF) muon-spin-relaxation (μSR) method for determining intrachain and interchain charge carrier hopping mechanisms. It is found that the depolarization rates at the low temperatures below 50 K indicate that the $H^{-0.5}$ field-dependent characteristics of the charge transport is dominated by mobility along the polymer chain (intrachain diffusion). With an increase in temperature, the charge carriers move perpendicular to the polymer chain (interchain diffusion), as characterized by the field dependence of depolarization rates of C-$H^{0.5}$ curve. The initial change in the carrier mobility appeared at around 50 K to 75 K.

Keywords: RR-poly(3-butylthiophene-2,5-diyl); LF-μSR; charge carrier diffusion

1. Introduction

Poly(3-alkylthiophene) (P3AT) has being intensively studied because the physical and chemical properties of this derivative can be effectively modified by varying the alkyl-side-chain length [1, 2, 3]. The study of alkyl-side-chain length dependent on field-effect mobility of holes, for example, showed that among the various alkyl-side-chain length, the poly(3-hexylthiophene) showed the highest value of field-effect holes mobility [3]. However, the origin of the observed non-linear dependence of field-effect holes mobility on the alkyl-side-chain length is not clearly understood yet.

The studies of temperature-dependent of charge carrier diffusion in P3AT with various alkyl-side-chain length have been of important research interest to provide information on intrinsic transport processes governing the mobility of charge carrier in the polymer chain [4]. Previously, we have studied temperature-dependent charge carrier diffusion in RR-poly(3-hexylthiophene-2,5-diyl) (RR-P3HT) [5] and RR-poly(3-octylthiophene-2,5-diyl) (RR-P3OT) [6] by performing LF-μSR measurements. From experimental results, it was found that the temperature-dependent charge carrier mobility exhibits a change of temperature "transition" from intrachain diffusion to interchain diffusion at 25 K

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and 50 K for RR-P3HT and RR-P3OT, respectively. This difference is assigned to the difference of distance between the chains [7]. It is clear that longer side chain leads to larger distance between the chains which implies in turn the need of large thermal energy to support the interchain hopping process.

Here, we report the temperature-dependent charge carrier diffusion in another alkyl-side-chain length of RR-poly(3-butylthiophene-2,5-diyl) (RR-P3BT) by the LF-μSR method for determining intrachain and interchain charge carrier hopping mechanisms in short alkyl-side-chain length.

2. Experimental

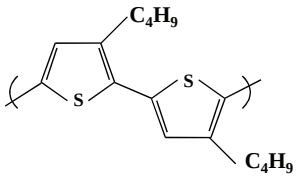

Figure 1: The chemical structure of poly(3-butylthiophene-2,5-diyl)

The RR-P3BT were obtained from Sigma-Aldrich. Figure 1 shows the chemical structure of poly(3-butylthiophene-2,5-diyl). The target consisted of the RR-P3BT sample wrapped in a 25 μm silver foil and mounted on a silver plate in the cryostat for muon spin relaxation measurements. The LF-μSR measurements were performed in magnetic field ranging from 0 to 395 mT and at temperature varied from 10 K to 300 K at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK using a pulsed positive surface muon beam [8, 9].

The longitudinal asymmetry parameter of μSR signal $A(t)$ at a time t is defined as $A(t) = [F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]$, where $F(t)$ and $B(t)$ are total muon events counted by the forward and backward counters, respectively, and α is the calibration factor reflecting the relative counting efficiencies between the forward and backward counters.

3. Results

For LF-μSR measurements in the conducting polymer samples, muons act as active probes. Implanted muon in the samples can pick up an electron and readily formed the muonium. Following rapid electronic and structural relaxation of the surrounding polymer, a negative polaron, a quasiparticle composed of an electron plus its accompanying polarization field, is formed. The polaron will move away from its initial site and diffuse up and down the polymer chain, giving rise to intrachain charge transport or hops between chains giving rise to interchain charge transport as well in the conducting polymer [10, 11, 12, 13].

Figure 2 shows the LF dependent variation of $A(t)$ at temperatures of 300 K and 10 K. $A(t)$ at both temperatures clearly displays field and temperature dependencies. The initial asymmetries increase with increasing field as a results of repolarization of the muonium states [14]. In order to obtain the detailed information of charge carrier diffusion on the polymers chain, all the time spectra were analyzed using the following two-component exponential function:

$$A(t) = A_1 exp(-\lambda_1 t) + A_2 exp(-\lambda_2 t) \quad (1)$$

where A_1 and A_2 are the initial asymmetries and λ_1 and λ_2 are corresponding the depolarization rates associated with the fast and slow components, respectively. According to Butler *et al.*, the LF dependence of the dynamical depolarization rate (λ) reflects the direction of the diffusion of the spin-excited state. That is, the depolarization rate is proportional to $H^{-0.5}$ for intrachain diffusion and C-$H^{0.5}$ for interchain diffusion [15].

Figure 3 shows the LF dependence of λ_1 in RR-P3BT at various temperature of 10 K, 25 K, 50 K, 75 K and 300 K. The data of 25 K, 50 K, 75 K and 300 K are shifted by multiplication of 2, 4, 50 and 100 respectively. At the low temperatures of 10 K, 25 K and 50 K, λ_1 indicates the $H^{-0.5}$ field-dependent characteristics of intrachain diffusion, implying that the charge transport is dominated by the mobility of the charge carriers along the polymer chain. With

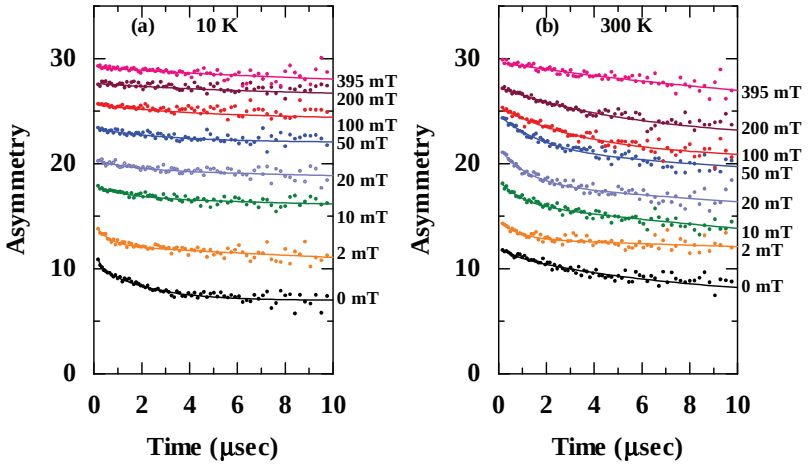

Figure 2: The Asymmetry data of RR-P3BT at (a) 10 K and (b) 300 K for various LF values. The solid lines are best fits to equation (1).

an increase in temperature, the charge carriers, which initially follow intrachain diffusion, move dominantly perpendicular to the polymer chain follow an interchain diffusion process, as characterized by the field dependence of λ_1, which could be well fitted by the C-$H^{0.5}$ curve, as shown in high temperatures of 300 K. The initial change in the carrier mobility appeared to have occurred at around 50 K to 75 K. A similar behavior was observed in the LF-dependent variation of λ_2. However, the values of λ_2 were two orders of magnitude smaller than those of λ_1.

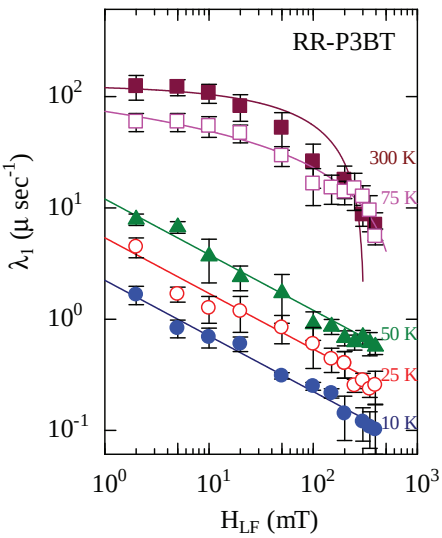

Figure 3: Longitudinal-field dependence of λ_1 of RR-P3BT at various temperatures. The data of 25 K, 50 K, 75 K and 300 K are multiplied by 2, 4, 50 and 100 respectively

From comparison between μSR data of RR-P3BT and that of RR-P3HT which is showing similar change in the direction of charge mobility at around 25 K to 50 K, it is found that interchain diffusion transport requires the assistance of higher temperature for RR-P3BT system. This difference may be due to the high concentration of P3BT rods, which makes a strong vertical phase separation[16], implying the need for higher thermal energy to support interchain hopping.

4. Conclusion

We have studied temperature-dependent of charge carrier diffusion in regioregular-poly(3-butylthiophene-2,5-diyl) by Longitudinal Field muon-spin-relaxation method for determining intrachain and interchain charge carrier hopping mechanisms. It is found that the depolarization rates at the low temperatures below 50 K indicate the field-dependent characteristics of the charge transport dominated by intrachain diffusion process. With an increase in temperature, the charge carriers move perpendicular to the polymer chain. The initial change in the carrier mobility appeared at around 50 K to 75 K.

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